PIXE analysis of PM10-2.5 and PM2.5 with hourly resolution from the Michelozzo's Courtyard in Palazzo Vecchio (Florence, Italy).

Available online at www.sciencedirect.com
SCIENCE DIRECT®
Nuclear Instruments and Methods in Physics Research B 249 (2006) 552–555
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

PIXE analysis of $PM_{10-2.5}$ and $PM_{2.5}$ with hourly resolution from Michelozzo's Courtyard in Palazzo Vecchio (Florence, Italy)

M. Chiari [a], F. Lucarelli [a], A. Migliori [a], S. Nava [a], G. Valli [b], R. Vecchi [b], I. Garcia-Orellana [c,*], F. Mazzei [d]

[a] Department of Physics, University of Florence and INFN, Sesto Fno. (FI), Italy
[b] Institute of General and Applied Physics, University of Milan and INFN, Milan, Italy
[c] University of Sevilla, Spain and University of Florence and INFN, Sesto Fno. (FI), Italy
[d] Department of Physics, University of Genoa and INFN, Genoa, Italy

Available online 24 May 2006

Abstract

The wall paintings of the Michelozzo's Courtyard (XVI century) at the main entrance of Palazzo Vecchio in Florence are in an advanced state of degradation. With the aim of understanding the environmental conditions in the Courtyard a wide research project has been instigated. In this study, the fine and coarse fractions of the PM_{10} have been collected by a 'streaker' sampler with an hourly resolution and then analysed by PIXE at the 3 MV tandetron accelerator in Florence; the first results will be presented here.

PACS: 89.60.−k; 89.90.+n; 82.70.Rr; 82.80.Ej

Keywords: Aerosol; PIXE; Hourly composition; Cultural heritage

1. Introduction

The high density of human activities in urban areas causes strong emissions of gaseous pollutants and particulate matter. The effects of air pollution on building materials and cultural heritage are currently of concern and are becoming more and more apparent both in outdoor and in indoor environments. The knowledge of the air quality in environments where artistic works are located as well as the understanding of how air pollutants affect materials are of interest; indeed, they are related with pollution control strategies in urban areas. In this context the study of air quality and the identification of pollution emission sources are mandatory.

Palazzo Vecchio (XIV century), located in the centre of the urban area of Florence, is the most important historical building of the town. The wall decorations of the portico in the main Courtyard (Michelozzo's Courtyard) were planned to be painted with the *good fresco* painting technique but most of them were finally executed using the *dry fresco* technique, which is considerably less durable than the former. The use of the dry technique, in addition to the environmental conditions and the high relative humidity in the Courtyard, caused the progressive weathering of the wall paintings, that lead to the necessary sequence of restorations that were carried out from the end of the eighteenth century. Indeed exfoliation and discoloration of the pigmented films are present in all the Courtyard decorations even though they were painted using different techniques.

In connection with a scheduled new restoration, the city council culture department has instigated an environmental investigation to study the causes of the wall decorations weathering. The attention in our research program has

* Corresponding author. Address: Centro Nacional de Aceleradores, Av. Thomas A. Edison s/n, E-41092 Sevilla, Spain. Tel.: +34 9544 60553; fax: +34 9544 60145.
E-mail address: iorellan@us.es (I. Garcia-Orellana).

0168-583X/$ - see front matter
doi:10.1016/j.nimb.2006.03.051

been focused to the wall painting of the Austrian city of Hall because of its anomalous and advanced deterioration, which can be observed at a glance because of a wide darkened central zone.

This paper will deal with preliminary results on particulate matter analyses and, particularly, on those obtained with hourly resolution. However, the research program involved different approaches as microclimate analysis, gaseous pollutant measurements, suspended particulate matter and dry deposition composition analysis as well as thermographic assessment.

2. Methods

A wintertime (12th December 2003–12th January 2004) and a summertime (22nd June–21st July 2004) sampling campaigns have been carried out in the Michelozzo's Courtyard of Palazzo Vecchio, Florence (Italy). $PM_{2.5}$ (particles with aerodynamic diameter $d_{ae} < 2.5$ μm) has been collected on a daily basis on Teflon filters (for elemental and soluble ion composition analysis) and on quartz fibre filters (for the organic and elemental carbon content determination) using two aerosol sequential CEN-equivalent samplers working in parallel. In addition, a 'streaker' sampler (PIXE Intl. Corp.) was employed for the collection of the fine ($d_{ae} < 2.5$ μm) and coarse (2.5 μm $< d_{ae} <$ 10 μm) fractions of PM_{10} with an hourly resolution [1]. All the aerosol samplers were placed at 3.5 m above floor, 3 m away from the Hall city painting.

Two pairs of streaker samples corresponding to the fine and coarse fractions from the winter and the summer campaigns were analysed by PIXE. Wintertime samples corresponded to two weeks (26th December 2003–9th January 2004) with two-hours resolution, while the summertime samples corresponded to one week (from 22nd to 28th of June 2004) with one-hour resolution.

The $PM_{2.5}$ mass concentration was gravimetrically determined on 24-h samples. These daily aerosol samples were analysed by ED-XRF for the elemental characterization, by ion chromatography for the determination of the ionic soluble component and by thermo-optical analysis (Sunset Laboratory Inc., USA) for the measurement of the elemental and organic carbon content. This information on the chemical composition is necessary to obtain the aerosol mass closure and to gain as complete a knowledge as possible of the chemical composition and to identify major emission sources of particulate matter. It is worthy noting that samples collected with a high temporal resolution are generally not suitable for mass determination, although their effectiveness in evidencing temporal patterns and the influence of episodic sources by means of hourly elemental analysis are of great value in environmental studies.

PIXE analysis has been performed at the 3 MV Tandetron accelerator in Florence, with a 20–30 nA 3 MeV proton beam using external beam set-up described in [2]. The measuring time per sample was about 3 min and the corresponding MDL ranged from about 1 ng/m^3 for the heaviest elements to 10–30 ng/m^3 (maximum) for the lighter ones.

Meteorological parameters and criteria pollutants, provided by the Meteorological Centre of Tuscany, were also included in data interpretation. Air mass back-trajectories, when necessary, have been calculated with the HYSPLIT model [3].

3. Results

$PM_{2.5}$ mass concentrations in the Courtyard ranged from 45 to 76 μg/m^3 during days with stable meteorological conditions in the winter campaign, but they decreased below 20 μg/m^3 because of strong winds and rains at the middle of the sampling period, and also possibly because the influence of the Christmas holidays. Summer $PM_{2.5}$ mass concentrations are on average lower than those of the winter campaign, ranging from 12 to 24 μg/m^3. The latter values are lower than wintertime ones with stable meteorological conditions, due to the higher atmospheric mixing layer heights typical of the warm season. It is note worthy that the mass concentrations registered in the Courtyard showed a temporal pattern and values very similar to those measured at different monitoring stations located within the urban area of Florence. This similarity suggests that the air quality in the Courtyard is comparable to the urban one implying that the heavy pollution loadings typical of the city will affect the decorations even though these are partially protected by the building. In addition, some effects of pollution might be enhanced in this peculiar environment: for example, particles deposited on walls (soiling effect) in outdoor environments are easily removed by wind and rain while underneath the portico in the Courtyard the atmospheric agents will not be so effective.

Fine and coarse average concentrations of more frequently detected elements are shown in Table 1 for the winter and summer streaker samples.

The soil-related elements such as Al, Si, Ca, Fe, Ti and Mn show a quasi-periodic temporal behaviour (Fig. 1) with higher concentrations during daylight/working hours and a decrease during the night, indicative of re-suspension due to anthropogenic activities, such as visiting periods, as well as to atmospheric daytime turbulence. Soil-related element concentrations on the other hand decrease significantly and have no modulation when Palazzo Vecchio was closed to visitors on the 1st January. The peak of soil-related elements corresponding to 05:00 on 29th December 2003 in the wintertime sampling period is seen in the coarse and fine fractions. Analysis of air mass back-trajectories revealed this could be attributed to saharan dust transport to florence. Although episodic, this is an additional, not negligible source of mineral dust, which may contribute to the soiling of wall paintings.

Cl and Na are always predominant in the coarse fraction and their concentration versus time trends in the coarse fraction during the winter are plotted in Fig. 2 where some

Table 1
Averaged concentrations (± standard deviation) in ng/m^3 of the most frequently detected elements of the fine and the coarse fractions collected with the streaker sampler during the winter and the summer campaigns

	Winter	Summer
Fine		
Na	62 ± 20	111 ± 37
Mg	54 ± 16	95 ± 34
Al	56 ± 26	150 ± 82
Si	137 ± 90	451 ± 213
S	360 ± 77	1197 ± 151
Cl	51 ± 29	71 ± 24
K	250 ± 53	227 ± 73
Ca	103 ± 42	310 ± 177
Ti	13 ± 3	23 ± 10
Mn	4 ± 1	5 ± 1
Fe	155 ± 109	193 ± 79
Ni	3 ± 2	3 ± 1
Cu	7 ± 5	5 ± 3
Zn	16 ± 7	13 ± 4
Pb	14 ± 10	24 ± 19
Coarse		
Na	165 ± 119	191 ± 115
Mg	71 ± 43	57 ± 34
Al	81 ± 77	58 ± 34
Si	266 ± 243	181 ± 104
S	81 ± 65	67 ± 32
Cl	147 ± 230	70 ± 102
K	64 ± 42	45 ± 22
Ca	325 ± 289	244 ± 159
Ti	12 ± 7	9 ± 4
Mn	4 ± 2	2 ± 1
Fe	175 ± 166	73 ± 49
Ni	2 ± 6	0.9 ± 0.2
Cu	6 ± 6	3 ± 2
Zn	6 ± 6	5 ± 3
Pb	2 ± 1	2 ± 1

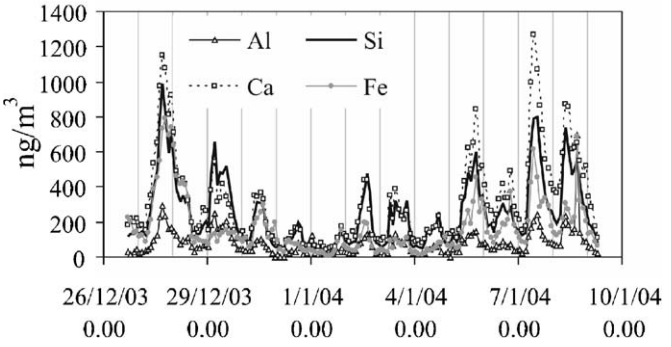

Fig. 1. Al, Si, Ca and Fe hourly concentrations (in ng/m^3) in the coarse fraction during the winter campaign.

peaks in Na and Cl temporal patterns can be observed. They are attributable to sea salt aerosol transported to Florence (the arrival of marine air masses has been confirmed by back-trajectories analysis). This is highly significant from a conservation point of view because sea salt, and particularly sodium chloride, may cause substantial weathering of porous building materials and surfaces of monuments; depending on the origin of the sea salt and local environment a number of different damage mechanisms can take place. During the monitoring campaigns Cl concentrations are generally quite low (see Fig. 2) but the presence of several peaks means that Cl contribution, although episodic, may be not negligible and its impact on wall painting decay should be considered.

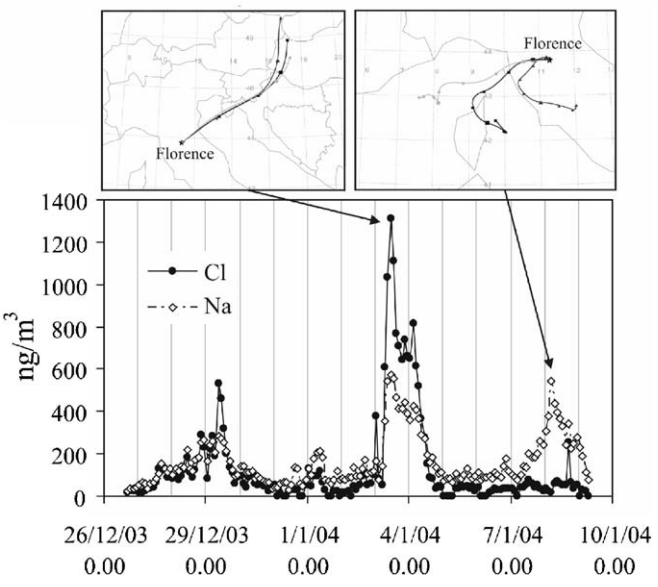

Fig. 2. Na and Cl concentrations (in ng/m^3) in the coarse fraction during winter campaign. Back-trajectories calculated with HYSPLIT model confirm the sea spray episodes.

Elements with a typical anthropogenic origin as Ni, Cu, Zn and Pb have been also detected in the Courtyard, with higher concentrations in the fine than in the coarse fraction, both in the winter and in the summer time.

In the fine fraction S is the most abundant element (average values are 0.36 μg/m^3 and 1.2 μg/m^3 in winter and summer, respectively). Its role in weathering is due to the acidic character of sulphates produced by the oxidation of gaseous SO_2, which reacts both with painted surfaces and with building materials [4,5].

The high temporal resolution of the samplings facilitated separation of a dominant background of S from superponed peaks. The background concentration is most likely due to a regional contribution, which can be estimated in about 1 μg/m^3 during the summer campaign, and about 300 ng/m^3 during the winter one (it is higher in summertime due to the more efficient photochemical activity in the atmosphere that favours secondary sulphates formation). This continuous S background suggests that the degradation process in the Courtyard, due to sulphates is always active. Superimposed S peaks are most probably due to sulphate production in the urban area.

During the authors previous investigations [6] many samples taken from the wall painting were analysed by SEM-EDS, micro-PIXE and binocular microscopy. These revealed a superficial blackening attributed to a soiling effect. The micro-PIXE analysis revealed the presence of sulphur in the plaster, decreasing from surface to inner layers, that might indicate a decay process on the superficial

layers of the dry painting due to the reaction of sulphur dioxide from atmosphere with moisture and the calcium carbonate of the plaster (the sulphation process involved a thickness of about 500 μm).

4. Conclusion

The $PM_{2.5}$ mass concentrations and temporal patterns measured in the Courtyard are comparable to those registered at different monitoring stations located in the urban area of Florence. Pollutants emitted by typical urban sources such as traffic, industrial emission and combustion processes have been detected in the ambient air of the Courtyard and they can heavily affect the ambient air in Courtyard. A non-negligible contribution from natural sources (sea salt, Saharan dust, resuspended soil dust) has been also detected. The observation of high sulphur concentration in the fine fraction of particulate matter is of interest because of its well-known role in weathering and sulphation.

Acknowledgement

This work has been financially supported by Italian Ministry of Education, University and Research in the framework of a wider research project (COFIN2003).

References

[1] A. D'Alessandro, F. Lucarelli, P.A. Mandò, G. Marcazzan, S. Nava, P. Prati, G. Valli, R. Vecchi, A. Zucchiatti, J. Aero. Sci. 34 (2003) 243.
[2] M. Chiari, F. Lucarelli, F. Mazzei, S. Nava, L. Paperetti, P. Prati, G. Valli, R. Vecchi, X-ray Spectrom. 34 (2005) 323.
[3] HYSPLT kindly provided by NOAA. Available from: <http://www.arl.noaa.gov/ready/hysplit4>.
[4] D. Camuffo, P. Brimblecombe, R. Van Grieken, H.J. Busse, G. Sturaro, A. Valentino, A. Bernardi, N. Blades, D. Shooter, L. De Bock, Kristin Gysels, Monika Wieser, Oliver Kim, Sci. Total Environ. 236 (1999) 135.
[5] P. Brimblecombe (Ed.), The Effects of Air Pollution on the Built Environment, Imperial College Press, 2002, p. 428.
[6] F. Giambi, Degree Thesis, University of Florence, 2003 (in Italian).